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(54) Nodular silver powder and process for preparing silver powder

(57) The invention is directed to silver powder comprising primary particles having a nodular shape a process for preparing silver powder, the powder obtained, the use of the powder for preparing silver containing layers and the products obtained by this use. The process comprises reducing silver ions in an aqueous solution containing nitrate, formate and citrate, at a temperature of at least 50°C.

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Nodular silver powder and process for preparing silver powder.

The present invention is directed to nodular silver powder and to a process for preparing silver powder. More in particular the invention is concerned with submicron nodular and submicron spherical silver powder and the production thereof.

Submicron silver particles are generally applied in the form of thick-film pastes. There are two types of thick-film pastes:

- high temperature thick-film pastes, and
- polymer thick-film paste.

The majority of the silver powders used in high temperature thick-film pastes has a spherical morphology. The pastes is applied to a ceramic substrate by screen printing. Subsequently the paste is dried and fired to remove all organic material and to obtain a sintered silver pattern.

The silver powders used in polymer thick film pastes have a flaky morphology. This paste is also applied to a substrate by screen printing. Subsequently the material is cured at a relatively low temperature During this curing the morphology of the material does not alter..Electrical conductivity is obtained by a physical contact between the individual silver flakes.

In general there are four main routes for the production of submicron silver powder. These route are:

- reduction of Ag^+ ions with an organic reducing agent
- reduction of Ag^+ ions with an inorganic reducing agent
- electrodeposition, and
- plasma techniques.

The present invention is mainly concerned with silver powder obtained by the first route, namely reduction of Ag^+ ions with an organic reducing agent.

The presently known routes for preparing silver powder are all directed at obtaining more or less spherical silver particles.

The present invention is directed to silver powder comprising primary particles having a nodular shape.

The amount of nodular particles in the powder is preferably at least 50 % by wt., more preferred at least 75 % and in particular 100 %.

The term 'nodular' as used herein defines particles having a largest size of 5 μm, preferably of 2 μm, whereas the aspect ratio is between 5 and 40. The aspect ratio is the ratio between the mean diameter and the mean thickness of the particle as determined by scanning electron microscopy.

According to the invention, the nodular silver powder has an aspect ratio in the range from 5 to 40. The thickness of the nodular particles can advantageously be between 50 and 100 nm, whereas the length thereof can preferably be at most 5 μm. The most preferred length is at most 2 μm, whereas the minimum length is preferably 0.5 μm.

For low temperature applications, such as conductive layers on substrates that cannot be sintered, the silver particles according to the invention, which have a rodlike and/or flaky morphology are advantageous. One of the advantages of the powder according to the invention is the fact that less powder is needed to obtain a good conductivity.

The nodular silver powder according to the invention can be prepared by a novel process comprising the reduction silver ions in an aqueous solution containing nitrate, formate and citrate, at a temperature of at least 50°C.

The invention is also directed to a process for producing silver powder by reducing silver ions in an aqueous solution containing silver ions, formate ions and citrate ions, at a temperature of at least 50°C. This process can either yield spherical or nodular particles, whereby the term 'nodular' is defined hereinabove.

The morphology of the powder depends in particular on the molar ratio's of the various ions in the reaction bath and on the temperature therein. Governing factors at a constant amount of silver ions added to the bath are the ratio of silver to formate, the ratio of citrate to silver and the temperature.

An important and advantageous aspect of the process of the present invention resides in the possibility to modify the properties of the product obtained by very small changes in the process conditions. This can be very important as usually a specific process can only yield particles within a small particle size range.

In the process of the present invention the preferred silver concentration is between 0.05 and 0.5 mol/liter, more in particular between 0.1 and 0.4 mol/liter. The molar ratio of formate to citrate ranges from 10/1 to 500/1. The molar ratio of silver ions to formate ranges from 1/10 to 2/1.

In a preferred embodiment of the invention, the reaction is carried out by preparing an aqueous solution of silver nitrate to which ammonium-formate and citric acid have been added in the form of an aqueous solution. This can either be one solution of both chemicals or two separate solutions. Preferably the solutions have been preheated to the required reaction temperature.

The reaction conditions are to be chosen in dependence of the required product properties, taking into account the various variables set out hereinabove. More in particular the reaction takes place in a stirred reactor at a temperature of between 50 and 125°C. More preferred temperatures are between 60 and 100°C.

The reaction bath is brought and/or kept at the required temperature for the time needed for completion of the reaction to the required product. Subsequently the silver powder produced is filtered off, or removed from the liquid in an other way. The silver powder can then be washed, dried,

comminuted and subjected to any further treatments necessary for obtaining the final product.

The silver powder thus obtained can then be mechanically comminuted into smaller agglomerates. The powders obtained have a low organic carbon residue.

The silver powders can be used for preparing inks and pastes, such as conductive pastes, which are used for preparing multilayer ceramics, ceramic capacitors, but also for conductive patterns on ceramic or polymeric substrates. In view thereof the present invention also covers the use of silver powders for preparing silve layers on various substrates, such as ceramic and polymeric materials and products thus obtained. Depending on the type of application, the applied film of silver powder containing paste is dried, and optionally sintered. This last embodiment is of course only possible when sinter resistant substrates have been used.

Suitable high temperature thick film paste compositions contain ethyl-cellulose, a glass-forming material, terpineol or comparable material and the silver powder, optionally in combination with other metal powders such as palladium.

Polymer thick film pastes usually comprise a thermoset polymeric material and a non-spherical silver powder.

The composition, which may contain other additives is prepared by mixing and/or milling the components to a paste. The paste is brought onto the surface of a substrate by suitable means, such as a sieve printing apparatus.

The printed material can subsequently be dried and depending on the use, be fired, resp. cured. Suitable firing temperatures are between 900 and 1100°C.

The present invention is now elucidated on the basis of some examples, which are not intended to limit the invention.

EXAMPLES

Silver nitrate was added to water in a 250 ml stirred reaction vessel (1250 rpm, axial stirrer) preheated to 70°C in an amount of 21 g/l of Ag^+. To this liquid an aqueous solution containing the required amount of ammonium-formate and citric acid, as indicated herebelow, which solution was also preheated to the reaction temperature, was added. The reaction was terminated after about 60 min. Spherical and nodular powders having various specific surface areas were obtained by variation of the ratio of citric acid to silvernitrate. The molar ratio of silver nitrate to ammonium formate was 1:7.5. The specific surface area was determined using nitrogen adsorption at one bar nitrogen partial pressure according to the method of Brunauer-Emmet-Teller, Metals Handbook, 9th ed. Vol. 7, Powder Metallurgy, pp. 262-267.

In the table the results of the various test have been given.

TABLE 1

Ag^+/citric acid (molar ratio)	Particle shape	SSA (m^2/g)	C-total (%, m/m)
1 : 2/3	A	5.2	0.15
1 : 1/2	A	6.0	0.36
1 : 1/3	A/B	6.3	0.27
1 : 1/4	A/B	5.6	0.16
1 : 1/8	A/B	4.0	0.11
1 : 1/16	B	4.1	0.28
1 : 1/32	B	3.9	0.35
1 : 1/64	B	1.8	0.11

A: Nodular

B: Spherical

A further set of experiments was carried out with a molar ratio of silver nitrate to ammonium formate of 1 : 2. The results were as follows.

TABLE 2

Ag^+/citric acid (molar ratio)	Particle shape	SSA (m^2/g)	C-total (%, m/m)
1 : 1/16	B	4.4	0.38
1 : 1/32	B	3.7	0.26
1 : 1/64	B	3.2	0.23

A third set of experiments was carried out with a molar ratio of silver nitrate to ammonium formate of 1 : 1. The results were as follows.

TABLE 3

Ag^+/citric acid (molar ratio)	Particle shape	SSA (m^2/g)	C-total (%, m/m)
1 : 1/32	B	3.7	0.35
1 : 1/64	B	3.6	0.27

CLAIMS T 1126 GBR

1. Silver powder comprising primary particles having a nodular shape.

2. Silver powder according to claim 1, wherein the mean largest size of the primary primary particles is at most 5 µm, preferably 2 µm.

3. Silver powder according to claim 1 or 2, wherein the aspect ratio is between 5 and 40.

4. Silver powder according to any one of the claims 1-3, wherein the thickness of the primary particles is between 50 and 100 nm.

5. Silver powder according to claim 1, substantially as described hereinbefore, especially with reference to the examples.

6. Process for preparing silver powder comprising reducing silver ions in an aqueous solution containing also formate and citrate, at a temperature of at least 50°C.

7. Process according to claim 6, wherein the silver concentration is between 0,05 and 0,5 mol, preferably between 0,2 and 0,3 mol.

8. Process according to claim 6 or 7, wherein the molar ratio of formate/citrate ranges from 10/1 to 500/1.

9. Process according to any one of claims 6-8, wherein the molar ratio of silver ions to formate ranges from 1/10 and 2/1.

10. Process according to any one of claims 6-9, wherein a solution of ammonium formate and citric acid is added to an aqueous solution of silver nitrate.

11. Process for preparing silver powder according to claim 6, substantially as described hereinbefore, especially with reference to the examples.

12. Silver powder prepared in accordance with the process of any one of claims 6-11.

13 Use of the silver powder according to any one of claims 1 to 5 and 12, for preparing silver containing layers.

14. Use according to claim 13, for preparing conductive patterns on ceramic or polymeric substrates and/or for preparing ceramic capacitors.

15. Use of silver powder according to claim 5, for preparing conductive patterns on polymeric substrates.

16. Products obtained by the use of silver powder according to claims 12-14.

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